In situ x-ray characterization and electron tomography study of ALD coatings in mesoporous thin films

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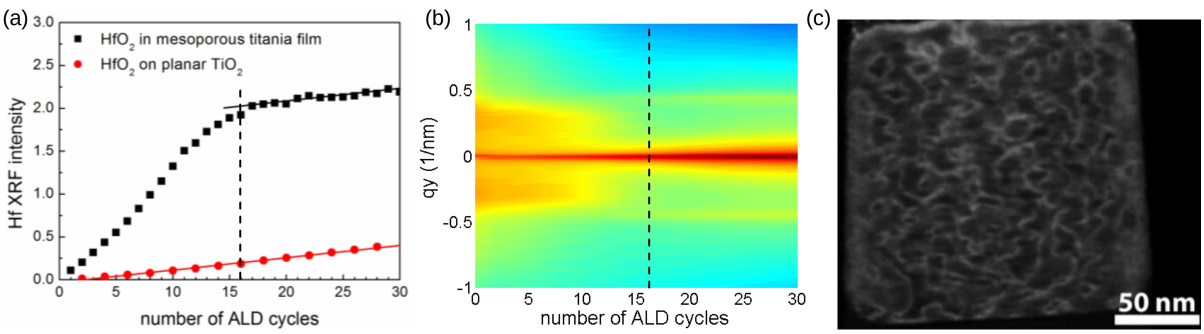
Mesoporous materials are of interest to a broad range of applications such as the development of optical, electronic and sensor devices and catalytic surfaces. For many of these applications, the interior surface of the porous material needs to be functionalized. ALD has become an attractive technique for tailoring porous materials because of its ability to produce conformal coatings. While the ALD modification of anodic aluminum oxide membranes with pore diameters of tens of nanometers has recently been investigated in detail,[1] only few authors have reported efforts to deposit and characterize ALD layers in mesopores with diameters < 10nm.

We present an *in situ* x-ray characterization[2] of HfO_2 ALD in mesoporous thin films along with an electron tomography study of the HfO_2 coating. Mesoporous titania films containing ink-bottle-type pores with ~6nm wide pore necks were coated with TEMAHf/H_2O ALD in an UHV chamber installed at the National Synchrotron Light Source at Brookhaven National Laboratory. X-ray fluorescence (XRF) and grazing incidence small angle x-ray scattering (GISAXS) measurements were performed every 1 and 2 ALD cycles, respectively. XRF measures the amount of deposited material, while GISAXS is sensitive to electron density fluctuations. Figure (a) shows the Hf XRF intensity against the number of cycles. During the first cycles, the intensity increased much faster in the mesoporous film than on a planar substrate, proving the penetration of HfO_2 into the porous material. After 16 cycles the growth rate in the porous film became similar to the growth rate on the planar substrate: the pores were no longer accessible for the TEMAHf precursor and ALD continued on top of the coated mesoporous film. Figure (b) shows the GISAXS spectrum (scattered intensity against q_y) as a function of the number of ALD cycles. During the first cycles, the shape of the spectrum changed due to a changing contrast in electron density. After 16 ALD cycles, the shape of the GISAXS spectrum became constant.

To support our interpretation of the XRF and GISAXS data, electron tomography was used to locate and visualize the HfO_2 layer in the mesoporous titania film. This technique allows to reconstruct the 3D structure from a series of 2D TEM images collected under different tilt angles.[3] The 3D reconstruction of the coated mesoporous film revealed that a ~3nm HfO_2 layer was conformally deposited throughout the porous film, confirming the XRF and GISAXS data. In order to visualize the 3D reconstruction, an orthogonal slice was made through the reconstruction (figure (c)): HfO_2 coating in light gray, titania pore walls in dark gray and open pores in black.



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